

R75-90

# Oxidation of Aromatic Amines and Diamines by OH Radicals. Formation and Ionization Constants of Amine Cation Radicals in Water

P. S. Rao and E. Hayon\*

Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760  
 (Received August 16, 1974; Revised Manuscript Received February 18, 1975)

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The one-electron oxidation by hydroxyl radicals of aromatic amines and diamines in water was studied using the fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry. The following compounds were examined: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), *p*-phenylenediamine (PD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD), *N,N,N',N'*-tetramethylbenzidine (TMB), and diphenylamine (DPA). The main initial reaction of the OH radicals is suggested to be an addition to these compounds to give absorption spectra which absorb strongly in the visible and uv regions. These OH radical adducts decay by first-order kinetics and have lifetimes of ~5–50 μsec, dependent on the pH, buffer concentration, and the nature of the aromatic amines and diamines. They decay to give species with somewhat similar absorption spectra and extinction coefficients, which are very long lived in the absence of oxygen. The latter species are assigned to the cation radicals TMPD<sup>•+</sup>, PD<sup>•+</sup>, DMPD<sup>•+</sup>, TMB<sup>•+</sup>, and DPA<sup>•+</sup>. The OH radical adducts and the cation radicals have acid-base properties. The *pK<sub>a</sub>* values of the cation radicals TMPDH<sup>2+</sup>, PDH<sup>2+</sup>, DMPDH<sup>2+</sup>, TMBH<sup>2+</sup>, and DPAH<sup>2+</sup> were found to be 5.3, 5.9, 6.1, 5.1, and 4.2, respectively. The results indicate that these aromatic amines and diamines can be oxidized by free radicals to yield the corresponding cation radicals.

## Introduction

The oxidation of aromatic amines in solution has been studied<sup>1,2</sup> by anodic electrochemistry using absorption spectrophotometry and ESR to observe and identify the intermediates produced in these organic redox systems. The ease of removal of electrons from the amino function makes it possible to study the oxidation reaction pathways of amines. The photochemistry<sup>3</sup> and radiation chemistry<sup>4</sup> of some aromatic amines, in particular *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), have so far been studied mainly in organic solvents.

Another pathway for the oxidation of aromatic amines and diamines which has not received much attention is via their reaction with oxidizing free radicals. We report below a study of the one-electron oxidation of some aromatic amines and diamines in water by hydroxyl radicals. The fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry was used to generate OH radicals and examine their subsequent reactions with these compounds.

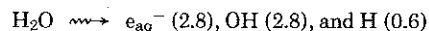
The following compounds have been examined: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), *p*-phenylenediamine (PD), *N,N*-dimethyl-*p*-phenylenedi-

amine (DMPD), *N,N,N',N'*-tetramethylbenzidine (TMB), and diphenylamine (DPA).

## Experimental Section

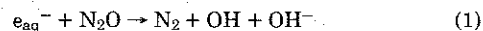
The pulse radiolysis equipment and experimental conditions employed have been described.<sup>5,6</sup> Single pulses of 2.3-MeV electrons and ~30-nsec duration were used.

The radiolysis of water produces



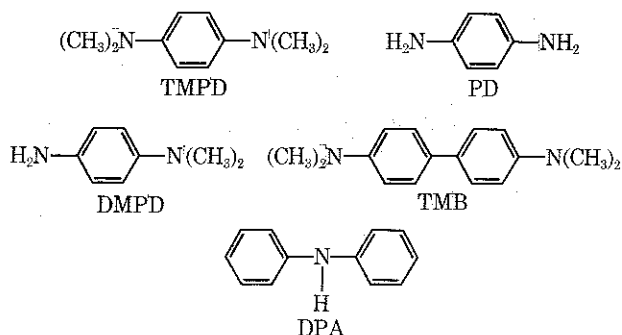
where the numbers in parentheses are the *G* values (number of radicals produced per 100 eV of energy absorbed).

All experiments were carried out in the presence of 1 atm of N<sub>2</sub>O (~2.2 × 10<sup>-2</sup> M) in order to convert the *e<sub>aq</sub>*<sup>-</sup> into OH radicals:



where *k*<sub>1</sub> = 8.7 × 10<sup>9</sup> M<sup>-1</sup> sec<sup>-1</sup> (ref 7). The OH radicals then react with the aromatic amines, as described below. The H atoms formed in the radiation chemistry of water presumably add to the benzene ring of these compounds to produce cyclohexadienyl type radicals, which usually absorb in the 350–400-nm region.

The chemicals used were the best research grade commercially available, and were purchased from Aldrich, Eastman Chemicals, K and K Laboratories, Mallinckrodt, and Baker and Adamson. They were used without further purification. Diphenylamine (Eastman and Aldrich) was recrystallized twice from methyl alcohol. Due to their ease of oxidation in solution, special care was taken to thoroughly degass the solutions before adding the amines and diamines. Exposure to room light and to the monitoring light from the xenon lamp used in the pulse radiolysis experiments was kept to a minimum. A synchronized shutter<sup>5</sup> and appropriate cut-off filters were also used.



**TABLE I: Reaction Rate Constants of  $e_{aq}^-$  with Aromatic Amines and Diamines in Water**

Amine	pH	$k, M^{-1} \text{ sec}^{-1}{}^a$
TMPD	8.0	$9.1 \times 10^7$
PD	9.0	$9.6 \times 10^7$
DMPD	9.0	$1.6 \times 10^8$
TMB	9.0	$1.7 \times 10^8$
DPA	9.2	$1.5 \times 10^9$

<sup>a</sup> Determined in the presence of  $\sim 0.5 M$  *t*-BuOH by monitoring the decay kinetics of  $e_{aq}^-$  at 700 nm.

Solutions were buffered using perchloric acid, potassium hydroxide, and  $\sim 1 \text{ mM}$  phosphate and borate buffers.

The extinction coefficients presented were derived using the  $G$  values given above and KCNS dosimetry.<sup>5</sup>

### Results and Discussion

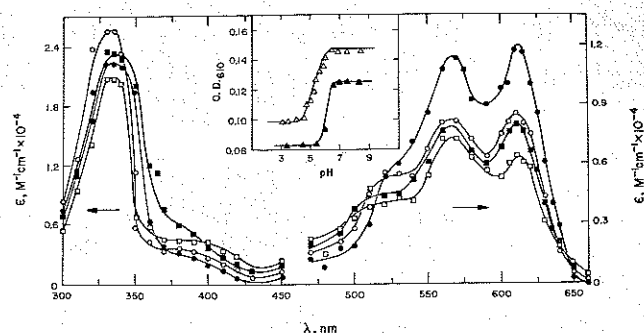
Aliphatic<sup>8</sup> and aromatic<sup>9</sup> amines are known to react relatively fast with OH radicals. The reaction rate constants increase on ionization of the  $-\text{NH}_3^+$  or  $-\text{NR}_2\text{H}^+$  groups. The reaction rate constants of  $e_{aq}^-$  with the aromatic amines and diamines examined in this work were not known. These rates were determined by following the decay kinetics of  $e_{aq}^-$  at 700 nm. The values obtained are given in Table I. The  $k(e_{aq}^- + \text{diphenylamine}) = 1.5 \times 10^9 M^{-1} \text{ sec}^{-1}$  is surprisingly high. Repurified material gave essentially the same value.

The concentrations of the amines and diamines used were chosen such that all ( $>95\%$ ) of the  $e_{aq}^-$  reacted with  $\text{N}_2\text{O}$ , reaction 1. All the experiments to be described below were carried out in the presence of 1 atm of  $\text{N}_2\text{O}$ .

*N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (TMPD). The reaction of OH radicals with TMPD (5 mM) at pH 3.2 produced, immediately after the 30-nsec pulse, intermediates which absorb strongly in the uv and visible regions, with maxima at  $\sim 335$ , 565, and 610 nm, see Figure 1. About 20–30  $\mu\text{sec}$  later, changes in absorbance were observed at most wavelengths. The new absorption spectrum has similar maxima at  $\sim 330$ , 565, and 610 nm, Figure 1, but different extinction coefficients. On reaction of OH radicals with TMPD at pH 8.0, the absorption spectrum of the initial intermediate also changes with time to give another species whose bands in the visible region have higher extinction coefficients, see Figure 1 and Table II. It should be pointed out that the change in absorbance with time increases at some wavelengths and decreases at other wavelengths. This indicates the presence of at least two transient species.

The second intermediates whose spectra are fully developed  $\sim 20$ –30  $\mu\text{sec}$  after the pulse are very stable (over periods of minutes, the time duration of the observation) so long as oxygen is not introduced in the system. These spectra resemble the spectrum of the  $\text{TMPD}^{\cdot+}$  cation radical (Wurster's blue) and have similar<sup>10</sup> maxima and extinction coefficients in the visible region.

The following mechanism is suggested: the OH radicals add to TMPD either to the aromatic ring or to the *N*-amine groups. Addition to the ring can occur at either an  $\alpha$  or  $\beta$  position to the amine. From the similarity of the spectra of the initial and final intermediates one cannot differentiate between the different possibilities. The addition reaction is represented by reaction 2. The initial intermedi-

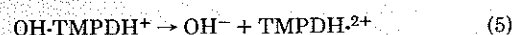
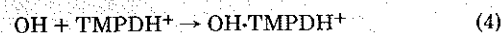


**Figure 1.** Optical spectra of intermediates produced from the reaction of OH radicals with tetramethyl-*p*-phenylenediamine (5 mM) in aqueous solution,  $\text{N}_2\text{O}$  (1 atm): (a) initial intermediate at pH 3.2 ( $\square$ ) and pH 8.0 ( $\blacksquare$ ); (b) second intermediate at pH 3.2 ( $\circ$ ) and pH 8.0 ( $\bullet$ ). Total dose  $\sim 1.2$  krad/pulse. Insert shows  $\Delta\text{OD}$  at 610 nm vs. pH for OH adduct ( $\blacktriangle$ ) and cation radical ( $\blacksquare$ ).

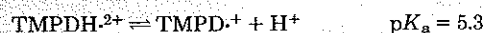
ate is suggested to be mainly the OH adduct. From the similarity of the spectrum of the second intermediate with the known spectrum of  $\text{TMPD}^{\cdot+}$ , loss of  $\text{OH}^-$  is suggested to occur:



In acid solutions, reactions 4 and 5 are suggested (protonation of one of the amines only is shown, since it is not known whether both amines are protonated under these conditions).



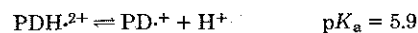
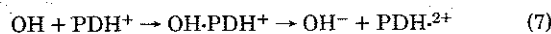
The absorbances of the initial and the second intermediates were measured at 610 nm as a function of pH. Titration curves are observed, from which  $\text{pK}_a$  values of 6.2 and 5.3 for the OH adduct and the cation radical, respectively, can be derived (see insert Figure 1). This shows for the first time the acid-base properties of amine cation radicals:



The rate constants of reactions 3 and 5 were determined, Table III, and are found to be  $\sim 8.0 \times 10^4$  and  $\sim 1.0 \times 10^5 \text{ sec}^{-1}$ , respectively. This small difference may not be significant, and may be dependent on the nature and concentration of the buffer used.

In support of the formation of  $\text{TMPD}^{\cdot+}$  from the oxidation of TMPD by OH radicals is the similarity of the absorption spectrum of  $\text{TMPD}^{\cdot+}$  and its extinction coefficients with those given in the literature.<sup>10</sup> For the 610–620-nm band,  $\epsilon$  values in various organic solvents ranging from  $1.3$  to  $2.0 \times 10^4 M^{-1} \text{ cm}^{-1}$  have been reported.<sup>10</sup> In this work, an  $\epsilon_{612}$  of  $1.2 \times 10^4 M^{-1} \text{ cm}^{-1}$  (Table II) was found in water.

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Solutions were buffered using perchloric acid, potassium hydroxide, and  $\sim 1$  mM phosphate and borate buffers.

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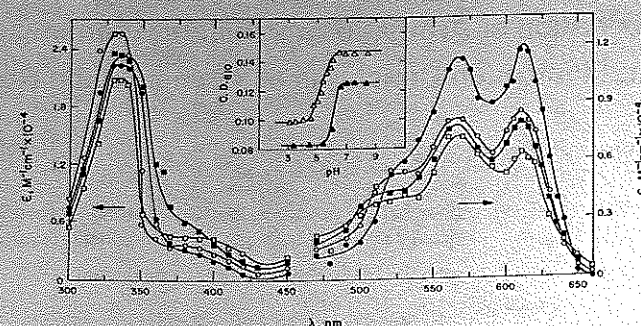
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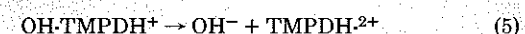
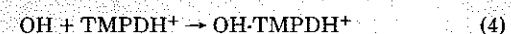


**Figure 1.** Optical spectra of intermediates produced from the reaction of OH radicals with tetramethyl-*p*-phenylenediamine (5 mM) in aqueous solution,  $N_2O$  (1 atm): (a) initial intermediate at pH 3.2 ( $\square$ ) and pH 8.0 ( $\blacksquare$ ); (b) second intermediate at pH 3.2 ( $\circ$ ) and pH 8.0 ( $\bullet$ ). Total dose  $\sim 1.2$  krad/pulse. Insert shows  $\Delta OD$  at 610 nm vs. pH for OH adduct ( $\blacktriangle$ ) and cation radical ( $\triangle$ ).

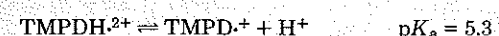
ate is suggested to be mainly the OH adduct. From the similarity of the spectrum of the second intermediate with the known spectrum of TMPD $^{+}$ , loss of  $OH^-$  is suggested to occur:



In acid solutions, reactions 4 and 5 are suggested (protonation of one of the amines only is shown, since it is not known whether both amines are protonated under these conditions).



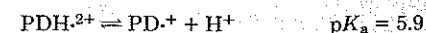
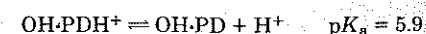
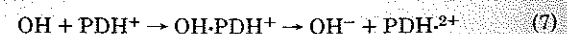
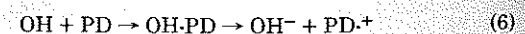
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The rate constants of reactions 3 and 5 were determined, Table III, and are found to be  $\sim 8.0 \times 10^4$  and  $\sim 1.0 \times 10^5 \text{ sec}^{-1}$ , respectively. This small difference may not be significant, and may be dependent on the nature and concentration of the buffer used.

In support of the formation of TMPD $^{+}$  from the oxidation of TMPD by OH radicals is the similarity of the absorption spectrum of TMPD $^{+}$  and its extinction coefficients with those given in the literature.<sup>10</sup> For the 610–620-nm band,  $\epsilon$  values in various organic solvents ranging from  $1.3$  to  $2.0 \times 10^4 M^{-1} \text{ cm}^{-1}$  have been reported.<sup>10</sup> In this work, an  $\epsilon_{612}$  of  $1.2 \times 10^4 M^{-1} \text{ cm}^{-1}$  (Table II) was found in water.

*p*-Phenylenediamine (PD). The reaction of OH radicals with *p*-phenylenediamine ( $pK_a = 3.3$  and 6.1) gave rise to intermediates which changed with time, as well as with pH (see Figure 2 and Table II). The sequence of reactions occurring are similar to those described above for TMPD:

**TABLE II: Absorption Maxima, Extinction Coefficients, and Ionization Constants of the OH Radical Adducts and Radical Cations of Aromatic Amines and Diamines in Aqueous Solution**

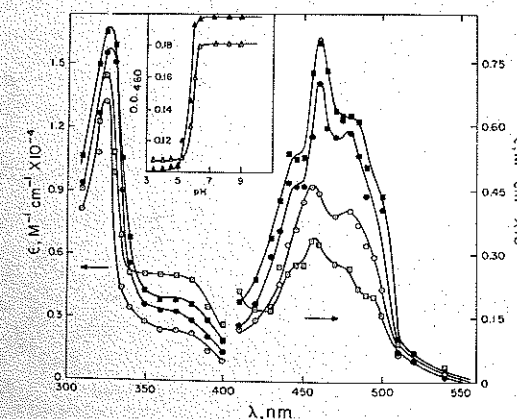
Amine <sup>a</sup>	p <i>K</i> <sub>a</sub> (radical)	OH adduct <sup>b</sup>				p <i>K</i> <sub>a</sub> (radical)	Cation radical <sup>b</sup>			
		Acid form		Base form			Acid form		Base form	
		λ <sub>max</sub>	ε	λ <sub>max</sub>	ε		λ <sub>max</sub>	ε	λ <sub>max</sub>	ε
TMPD	6.2	335	2.0 × 10 <sup>4</sup>	340	2.3 × 10 <sup>4</sup>	5.3	330	2.5 × 10 <sup>4</sup>	335	2.3 × 10 <sup>4</sup>
		565	7.4 × 10 <sup>3</sup>	570	8.1 × 10 <sup>3</sup>		565	7.8 × 10 <sup>3</sup>	570	1.1 × 10 <sup>4</sup>
		610	8.2 × 10 <sup>3</sup>	610	1.2 × 10 <sup>4</sup>		610	8.6 × 10 <sup>3</sup>	612	1.2 × 10 <sup>4</sup>
PD (3.3, 6.1)	5.9	325	1.4 × 10 <sup>4</sup>	325	1.7 × 10 <sup>4</sup>	5.9	325	1.3 × 10 <sup>4</sup>	325	1.6 × 10 <sup>4</sup>
		455	4.6 × 10 <sup>3</sup>	460	7.8 × 10 <sup>3</sup>		455	4.7 × 10 <sup>3</sup>	460	7.1 × 10 <sup>3</sup>
				480	6.4 × 10 <sup>3</sup>		480	4.0 × 10 <sup>3</sup>	480	5.8 × 10 <sup>3</sup>
DMPD		330	9.0 × 10 <sup>3</sup>			6.1	330	1.2 × 10 <sup>4</sup>		
		510	3.0 × 10 <sup>3</sup>	515	5.4 × 10 <sup>3</sup>		515	7.3 × 10 <sup>3</sup>	515	5.2 × 10 <sup>3</sup>
		560	3.0 × 10 <sup>3</sup>	560	5.2 × 10 <sup>3</sup>		560	6.3 × 10 <sup>3</sup>	560	5.5 × 10 <sup>3</sup>
TMB <sup>c</sup>						5.1	470	1.2 × 10 <sup>4</sup>	470	3.8 × 10 <sup>3</sup>
							700	1.6 × 10 <sup>3</sup>	700	8.0 × 10 <sup>2</sup>
DPA (0.8)	4.2	335	1.6 × 10 <sup>4</sup>	325	6.5 × 10 <sup>3</sup>	4.2	335	1.3 × 10 <sup>4</sup>	320	1.5 × 10 <sup>4</sup>
		670	8.0 × 10 <sup>4</sup>	670	6.0 × 10 <sup>3</sup>		675	8.0 × 10 <sup>3</sup>	700	1.2 × 10 <sup>3</sup>
				675	2.0 × 10 <sup>3</sup>					

<sup>a</sup> See text for list of compounds; values in parentheses are  $pK_a$ . <sup>b</sup> Wavelength given in nm units and  $\epsilon$  in  $M^{-1} \text{ cm}^{-1}$ ;  $\epsilon$  values derived assuming  $[\text{radical}] = [\text{OH}]$ , see text. <sup>c</sup> Mixture of OH adduct and cation radical probably present (see text).

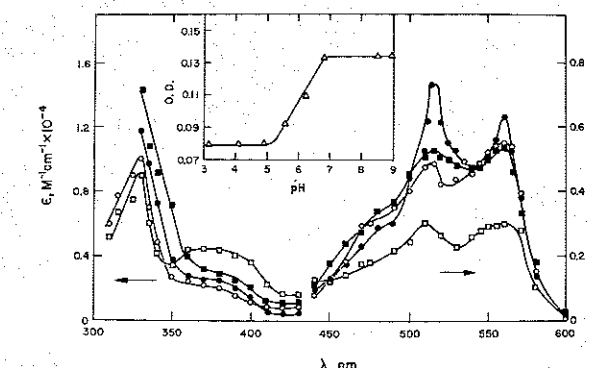
**TABLE III: Rate of Formation of Radical Cations from the Decay of the OH Radical Adducts to Aromatic Amines and Diamines in Water**

Amine <sup>a</sup>	pH	Wavelength monitored, nm	$k, \text{ sec}^{-1}$
TMPD	3.2	370; 610	$1.0 \times 10^5$
	8.0	610	$8.0 \times 10^4$
PD	3.5	370	$3.0 \times 10^5$
	9.0	370; 480	$6.0 \times 10^4$
DMPD	3.2	545	$6.0 \times 10^4$
	8.0	350	$5.0 \times 10^4$
TMB	3.5	475	$1.0 \times 10^5$
	9.2	450	$2.0 \times 10^5$
DPA	3.0	320	$1.0 \times 10^5$
	9.0	320	$2.0 \times 10^5$

<sup>a</sup> See text for list of compounds.



**Figure 2.** Optical spectra of intermediates produced from the reaction of OH radicals with *p*-phenylenediamine (2 mM) in aqueous solution,  $N_2O$  (1 atm): (a) initial intermediate pH 3.2 ( $\square$ ) and pH 8.0 ( $\blacksquare$ ); (b) second intermediate at pH 3.2 ( $\circ$ ) and pH 8.0 ( $\bullet$ ). Total dose  $\sim 2.0$  krad/pulse. Insert shows  $\Delta OD$  at 460 nm vs. pH for OH adduct ( $\blacktriangle$ ) and cation radical ( $\triangle$ ).



**Figure 3.** Optical spectra of intermediates produced from the reaction of OH radicals with *N,N*-dimethyl-*p*-phenylenediamine (2 mM) in aqueous solution,  $N_2O$  (1 atm): (a) initial intermediate at pH 3.2 ( $\square$ ) and pH 8.0 ( $\blacksquare$ ); (b) second intermediate at pH 3.2 ( $\circ$ ) and pH 8.0 ( $\bullet$ ). Total dose  $\sim 1.5$  krad/pulse. Insert shows  $\Delta OD$  at 350 nm vs. pH for OH adduct ( $\blacktriangle$ ) and cation radical ( $\triangle$ ).

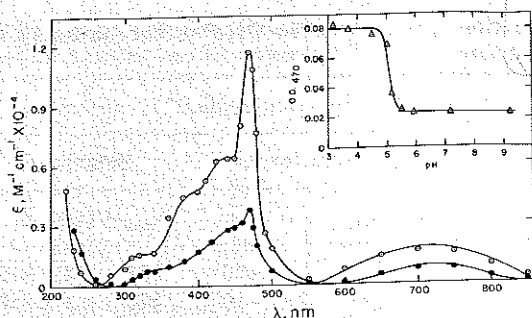
The spectrum of the PD $^{+}$  cation radical observed is quite similar to that observed in ethanol.<sup>10</sup> The  $\epsilon$  values in the literature for the 460-nm band are, however, higher by a factor  $\geq 3.0$ . No explanation can be offered at present for this difference.

The rates of decay of the initial intermediate to form the second radical are given in Table III. Values of  $3.0 \times 10^5$  and  $6.0 \times 10^4 \text{ sec}^{-1}$  at pH 3.5 and 9.0 were observed.

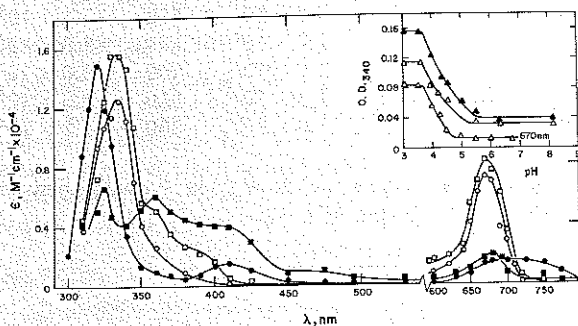
*N,N*-Dimethyl-*p*-phenylenediamine (DMPD). With DMPD ( $pK_a = 2.85$ ), because the molecule is not symmetric the reaction of OH radicals can produce more than one isomer. The initial OH adduct spectra at pH 3.2 and 8.0, as well as the corresponding cation radical spectra, are shown in Figure 3 and Table II. The spectrum of the DMPD $^{+}$  radical cation is in general agreement with that reported in the literature.<sup>10</sup>

The ionization constant of the DMPDH $^{2+}$  radical is  $\sim 6.1$ :





**Figure 4.** Optical spectra of intermediates produced from the reaction of OH radicals with  $N,N,N',N'$ -tetramethylbenzidine ( $2 \times 10^{-4}$  M) in aqueous solution,  $N_2O$  (1 atm) at pH 3.5 (O) and pH 9.2 (●). Total dose  $\sim 1.5$  krad/pulse. Insert shows  $\Delta OD$  at 470 nm vs. pH. Extinction coefficients may be low (see text).



**Figure 5.** Optical spectra of intermediates produced from the reaction of OH radicals with diphenylamine ( $2 \times 10^{-4}$  M) in aqueous solution,  $N_2O$  (1 atm): (a) initial intermediate at pH 3.0 (□) and pH 9.0 (■); (b) second intermediate at pH 3.0 (O) and pH 9.0 (●). Total dose  $\sim 1.5$  krad/pulse. Insert shows  $\Delta OD$  at 340 and 670 nm vs. pH for OH adduct (▲) and cation radical (Δ, Δ). Extinction coefficients low (see text).

*N,N,N',N'*-Tetramethylbenzidine (TMB). The reaction of OH radicals with TMB can produce different OH adducts which may not all lead to the formation of the  $TMB^{\cdot+}$  radical cation. Hence the spectrum shown in Figure 4 may contain bands which do not represent the absorption spectrum of  $TMB^{\cdot+}$ . The main absorption maximum at  $\sim 470$  nm probably represent  $TMB^{\cdot+}$ . It also agrees with a recently reported<sup>11</sup> spectrum for this cation radical. The ESR spectrum has also been examined.<sup>12</sup> The extinction coefficients given in Table II may be too low since a fraction of the OH radicals do not oxidize TMB to form  $TMB^{\cdot+}$ .

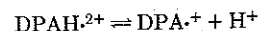
A  $pK_a \sim 5.1$  was observed for the dissociation of  $TMBH^{2+}$ , see Figure 4 and Table II.

*Diphenylamine (DPA)*. As discussed above for TMB, some of the OH radicals reacting with diphenylamine ( $pK_a = 0.79$ ) produce adducts which do not probably form the  $DPA^{\cdot+}$  cation radical.

The spectra of the initial and second intermediates at

pH 3.0 and 9.0 are shown in Figure 5 and Table II. The  $DPA^{\cdot+}$  radical cation is reported<sup>10</sup> to have bands with maxima at 350 and 660–680 nm, in reasonable agreement with the spectrum shown in Figure 5. The extinction coefficients given in Table II are considered to be too low since only a fraction of the OH radicals form  $DPA^{\cdot+}$ .

A  $pK_a = 4.2$  has been observed for



The rates of decay of the initial intermediate to form the cation radicals are  $1.0 \times 10^5$  and  $2.0 \times 10^5 \text{ sec}^{-1}$  at pH 3.0 and 9.0, respectively, see Table III.

## Conclusions

The main reaction of OH radicals with aromatic amines and diamines in water was shown to form initially an OH radical adduct. These OH adducts have a lifetime of 5–50  $\mu\text{sec}$ , dependent on the nature of the amines, the pH of the experiment, and the buffer concentration. They decay by a first-order process to generate the corresponding cation radicals. These cation radicals have acid-base properties and their ionization constants have been determined. With some compound, the OH adducts do not appear to form quantitatively the corresponding cation radicals. Furthermore, due to the similarity in the absorption spectra of the initial and second intermediates formed in these systems, one cannot exclude the possibility of some direct formation of cation radicals via an electron transfer from the amines to OH radicals.

In addition to the well-known oxidation of aromatic amines and diamines in electrochemistry, photochemistry, and radiation chemistry, the above results indicate that the reaction of these compounds with certain free radicals can also lead to their oxidation.

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